REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	5/1/97	1 Nov 1993 -- 31 Dec 1996

4. TITLE AND SUBTITLE

First-Principles Calculations for Ferroelectrics

5. FUNDING NUMBERS

Contract Number:
N00014-94-1-0044

R&T Project Number:
fmod007---07

6. AUTHOR(S)

Henry Krakauer

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

Dept. of Physics, P.O. Box 8795,
College of William and Mary,
Williamsburg, VA 23187-8795

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

Office of Naval Research

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

a. DISTRIBUTION / AVAILABILITY STATEMENT

12. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

First-principles calculations for ferroelectrics reveal the existence of extended instabilities as a function of wavevector in KNbO3 and SrTiO3. The scope of the first-principles results is extended through the use of effective Hamiltonians, determined with no empirical or experimental input, using a database of first-principles calculations. Molecular dynamics simulations using these effective Hamiltonians then predict ferroelectric phase transition temperatures, phonon softening, and diffuse X-ray scattering behavior. These calculations also demonstrate for the first time the existence of pre-formed dynamic precursor chain-like structures in KNbO3 and BaTiO3, well above the ferroelectric transition temperatures.

14. SUBJECT TERMS

Ferroelectrics, first-principles calculations, density functional theory, LAPW method, linear response

15. NUMBER OF PAGES

8

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

A. Description and Motivation of the Scientific Research Goals

There are many experimental indications in perovskite ferroelectrics that the actual atomic structure may be significantly different locally than is indicated by the average crystallographic structure deduced from elastic X-ray and neutron scattering. Perhaps the earliest evidence is from diffuse X-ray scattering measurements,[1] where temperature-dependent streak patterns were interpreted in terms of precursor short-range order in the form of static chains of distorted primitive cells along [100] directions. Observations of quasi-elastic central peaks in neutron scattering[2] and Raman spectroscopy[3] above the phase transition temperature were also indicative of preformed clusters of the low temperature phase. More recently, pair distribution functions obtained from neutron scattering measurements[4] up to very high momentum transfers and XAFS measurements[5] indicate the presence of short-range order. This motivated our detailed study of the real-space character of instabilities in these materials.

While the first-principles calculations carried out in this grant period provide a great deal of information, they are limited to zero temperature. We can extend the scope of the first-principles methods through the use of *ab initio* effective Hamiltonians, H_{eff},[6] which are constructed from the results of the first-principles calculations. These first-principles methods, comprising total energy and force techniques such as the LAPW method and a first-principles LAPW linear response method developed in my group provide detailed information about the electronic bonding, atomic geometry, and vibrational properties of these materials. The effective Hamiltonians are constructed by removing the inessential degrees of freedom, while requiring that they reproduce the low-energy Born-Oppenheimer surface as determined by the first-principles results. Using a database of first-principles LAPW total-energy and linear response calculations, the important degrees of freedom can be obtained (these are essentially the local soft-mode coordinates) and then the parameters of H_{eff} can be fitted. We then use H_{eff} to perform classical molecular dynamics (MD) simulations as a function of temperature. The MD simulations thus complement the first-principles method, allowing us to perform constant temperature and pressure simulations, where the volume and shape of the unit cell can vary. The MD simulations enable us

---

1 R. Comes, M. Lambert and A. Guinier, *Sol. State Commun* **6**, 715 (1968).

2 S. M. Shapiro, J. D. Axe and G. Shirane, *Phys. Rev. B* **6**, 4332 (1972).

3 M. D. Fontana, H. Idrissi, G. E. Kugel and K. Wojcik, *J. Phys. Condens. Matter* **3**, 8695 (1991).

4 S. Teslic, T. Egami and D. Viehland, *J. Physics and Chem. Solids* **57**, 1537 (1996).

5 E. A. Stern and Y. Yacoby, *J. Physics and Chem. Solids* **57**, 1449 (1996).

6 W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phys. Rev. Lett.* **73**, 1861 (1994); K. M. Rabe and U. V. Waghmare, *Phys. Rev. B* **52**, 13236 (1995).

to predict ferroelectric transition temperatures, phonon softening, and to identify and characterize precursor local structures.

B. Significant Results [Note: references in square brackets refer to publications in Section D.]

Although $KNbO_3$ is one of the most extensively studied ferroelectrics, the character of its ferroelectric phase transitions (and those of related systems like $BaTiO_3$) has continued to be a subject of controversy. Previous density functional total energy calculations found $q = 0$ instabilities providing qualitative support for the order-disorder scenario. We have discovered that the instabilities of $KNbO_3$ (and most likely those of related perovskite ferroelectrics) are considerably more complex than previously suspected, in a way that may explain and reconcile some of the apparently contradictory experimental results. [1, 2] The principal results found in the ideal $KNbO_3$ perovskite structure are i) the system is *stable* against displacements of a single Nb atom, and ii) unstable TO modes exist for q along the [100] directions. Based on an analysis of the wavevector dependence of the lattice instabilities, we proposed [2, 3, 5] a real-space chain-like instability and a scenario of sequential "freezing" out or onset of coherence of these instabilities, which qualitatively explains the sequence of observed temperature-dependent ferroelectric phases in $KNbO_3$. We suggested that this chain-like instability should also be found in $BaTiO_3$. Motivated by this suggestion, Ghosez *et al.*[7] recently carried out a similar study for $BaTiO_3$ and confirmed this.

We wanted to further study and characterize these precursor chain-like disordered structures in perovskite ferroelectrics. By precursor structures we mean locally-ordered atomic structures that are already present above the ferroelectric phase transition temperature. To do this, we performed molecular dynamics calculations on $KNbO_3$ and $BaTiO_3$ using effective Hamiltonians.[9] These calculations reproduce the diffuse x-ray scattering measurements of Comes *et al.*, showing that these disordered chain-like correlations really exist and "freeze" out as we had proposed [2, 3, 5]. Our discovery of the existence of disordered chain-like correlations in these materials provides for the first time an *ab initio* microscopic basis for the empirical static-chain model that was used by Comes *et al.* to interpret their diffuse x-ray scattering measurements.

Although a model based on static chains explains the pattern of streaks observed in x-ray scattering, it is not the only explanation. Dynamical fluctuations of the chain-like correlations could also account for these patterns. Indeed, preliminary results [9] indicate a long-lived dynamic character of these chain-like structures. The MD simulations show that the chains are preformed well above the cubic-tetragonal phase transition temperature. These chains are rows of distorted primitive cells oriented along the three cubic axes, with the atomic displacements along the chain highly correlated with one other. Displacements in different chains are uncorrelated at high

---

[7] P. Ghosez, X. Gonze and J.-P. Michenaud, *Ferroelectrics*, in press.

temperature, and the observed phase transitions correspond to the sequential freezing or onset of coherence of families of chains along the three cubic axes. These preliminary results show for the first time that *dynamic* low-frequency chain-like structures are precursors of the ferroelectric phase transitions in $KNbO_3$ and $BaTiO_3$.

By contrast with $KNbO_3$ and $BaTiO_3$, no ferroelectric phases have been observed in $SrTiO_3$ down to the lowest temperatures measured. To understand these different behaviors we have carried out a linear response study of the lattice dynamics of cubic $SrTiO_3$ [6]. We correctly obtain the known instability at the R-point in the Brillouin zone (BZ), which is responsible for the antiferrodistortive phase transition to the tetragonal structure at about 105 K. Moreover, we found that this antiferrodistortive instability extends along the entire R-M-R line in the BZ, forming a one-dimensional cylindrical tube in the BZ. We also found that this instability competes with a "ferroelectric" instability centered at q = 0, whose phase space is considerably reduced compared to $KNbO_3$. The extended character of the antiferrodistortive instability in momentum space suggests the possibility of real-space locally ordered precursors. The one-dimensional character in momentum space of the antiferrodistortive instability corresponds to real-space planar instabilities characterized by rotations of oxygen octahedra. Future molecular dynamics calculations will be needed to further investigate these structures.

In related studies, [7, 8] we also examined the variation of the Born effective charges and dielectric constant in going from the cubic to the tetragonal and ground-state rhombohedral phases in $KNbO_3$. The Born effective charges in the cubic perovskite ferroelectrics are anomalously large, and this is related to the mixed ionic/covalent character of the chemical bonding in these materials and to the existence of the ferroelectric instabilities. Since the electromechanical properties depend sensitively on these quantities, it is very important to study their structural dependence. The ground state structure of $KNbO_3$ in the rhombohedral phase was determined and found to be in good agreement with experiment. In the course of this study, we also found a very large polarization dependence of the Born effective charge and dielectric constant. Contrary to previous claims in the literature, we found rather large (order of 10% or greater) changes in these quantities. Such sensitive structural-dependence has been suggested in non-ferroelectric SiC as well. This motivated our study of the pressure dependence of the Born Effective charges, dielectric constant and lattice dynamics in SiC, [4] where a recent publication claimed to observe a strikingly anomalous pressure dependence of the Born effective charge in SiC. By contrast with ferroelectric $KNbO_3$, we found an unremarkable small linear volume dependence of this quantity. We were able to attributed the experimentalist's conclusions to their use of an incorrect assumed scaling relation for the pressure dependence of the dielectric constant, which we were able to correctly calculate.

C. Impact of this Work on Future Research

The most important outcome of our research is the demonstration of the existence of dynamic precursor chain-like structures in $KNbO_3$ and $BaTiO_3$. Our molecular dynamics

simulations using effective Hamiltonians (exclusively constructed from the first-principles results), demonstrate for the first time the existence of pre-formed precursor dynamic chain-like structures well-above the ferroelectric transition temperatures. Future research in these and related materials will have to consider the role of these structures on the electromechanical properties of these materials. We plan to investigate their role, for example, in the newly discovered single crystal relaxor ferroelectrics.

D. List of Publications/Reports/Presentations Under This Grant

Papers Published in Refereed Journals

1) "Lattice Dynamics of Ferroelectrics Using the LAPW Linear Response Method: Application to $KNbO_3$," R. Yu, C.-Z. Wang, and H. Krakauer, *Ferroelectrics* **164**, 161 (1995).

2) "First-Principles Determination of Chain-Structure Instability in $KNbO_3$," R. Yu and H. Krakauer, *Phys. Rev. Lett.* **74**, 4067 (1995).

3) *"Ab Initio* Linear Response Calculations of Lattice Dynamics Using an LAPW Basis," H. Krakauer, R. Yu and C.-Z. Wang, *Inter. Jour. Quant. Chem.: Quant. Chem. Symp.* **29**, 131 (1995).

4) "Pressure Dependence of Born Effective Charges, Dielectric Constant, and Lattice Dynamics in SiC," C.-Z. Wang, R. Yu and H. Krakauer, *Phys. Rev. B* **53**, 5430 (1996).

5) "Wavevector Dependence of Ferroelectric Instabilities in $KnbO_3$," H. Krakauer, R. Yu, and C.-Z. Wang, *J. Phys. Chem. Sol.* **57**, 1409 (1996).

6) "*Ab Initio* Linear Response Study of $SrTiO_3$," C. LaSota, C.-Z. Wang, R. Yu, and H. Krakauer, *Ferroelectrics*, in press.

7) "Born Effective Charges, Dielectric Constants, and Lattice Dynamcis of $KnbO_3$," C.-Z. Wang, R. Yu, and H. Krakauer, *Ferroelectrics*, in press.

8) "Polarization Dependence of the Born Effective Charge and Dielectric Constant in $KnbO_3$," C.-Z. Wang, R. Yu, and H. Krakauer, *Phys. Rev. B* **54**, 11161 (1996).

9) "Precursor Structures in Ferroelectrics from First-Principles Calculations," H. Krakauer, R. Yu, C.-Z. Wang, and C. LaSota, *Ferroelectric*, in press.

Presentations - Invited

1) *Workshop on First-Principles Calculations for Ferroelectricity*, February 1994: "Lattice Dynamics of Ferroelectrics Using the LAPW Linear Response Method: Application to $KNbO_3$," R. Yu, C.-Z. Wang, and H. Krakauer.

2) *3rd Williamsburg Workshop on Fundamental Experiments in Ferroelectrics*, Feb. 5-8, 1995, Williamsburg, VA. "Wavevector Dependence of Ferroelectric Instabilities in $KNbO_3$," H. Krakauer, R. Yu, and C. Z. Wang.

3) *1995 Sanibel Symposium*, Feb 25-Mar. 4, 1995, St. Augustine, Florida. *"Ab Initio* Linear Response Calculations of Lattice Dynamics Using an LAPW Basis," H. Krakauer, R. Yu, and C. Z. Wang.

4) *Electronic Structure Theory Workshop, Univ. of California, Davis*, Mar. 17-19, 1995. "Wavevector dependence of Ferroelectric Instabilities in $KNbO_3$," Henry Krakauer.

5) *Symposium of the Division of Computational Physics, "Advances in Computational Materials Science," American Physical Society Meeting*, Mar. 20-24, 1995, San Jose, California. "*Ab Initio* Linear Response Calculations of Lattice Dynamics Using and LAPW Basis," Henry Krakauer.

6) *7th Annual Workshop on Recent Developments in Electronic Structure Algorithms*, May 19-22, 1995, St. Mary's College, St. Mary, MD. "LAPW Linear Response Calculations of Ferroelectric Instabilities in $KNbO_3$," Henry Krakauer.

7) *Centre European de Calcul Atomique et Moleculaire (CECAM) Workshop on "First-Principles Theory of Polarization, Fields, and Currents in Insulators,"* July 10-13, 1995, Lyon, France. "Wavevector Dependence of Ferroelectric Instabilities in $KNbO_3$," Henry Krakauer.

8) *Materials Modeling, Naval Research Laboratory*, Oct. 17-18, 1996, Washington, D.C. "*Ab Initio* Linear Response Calculations of Lattice Dynamics," H. Krakauer.

9) *4th Williamsburg Workshop on First-Principles Calculations for Ferroelectrics*, Feb. 4-7, 1996, Williamsburg, VA. "*Ab Initio* Linear Response Study of $SrTiO_3$," C. LaSota, C. Z. Wang, R. Yu, and H. Krakauer.

10) *4th Williamsburg Workshop on First-Principles Calculations for Ferroelectrics*, Feb. 4-7, 1996, Williamsburg, VA. "First-Principles Calculations of Structural and Dynamical Properties of $KnbO_3$," C. Z. Wang, R. Yu, and H. Krakauer.

11) *Centre European de Calcul Atomique et Moleculaire (CECAM) Workshop on "Ab Initio Phonons Workshop,"* July 1-3, 1996, Lyon, France. "*Ab Initio* Linear Response Studies of $KnbO_3$ and $SrTiO_3$," Henry Krakauer.

E. Participants and Status

Henry Krakauer - PI, Professor of Physics

Rici Yu - Postdoctoral Researcher

Christopher LaSota Graduate Student [supported by a DOD "Augmentation Award for Science and Engineering Research Training (AASERT)" N00014-93-1095 to this grant.